Supporting Information

for

Pilot-Scale Ozone/Biological Activated Carbon Treatment of Reverse Osmosis Concentrate: Potential for Synergism Between Nitrate and Contaminant Removal and Potable Reuse

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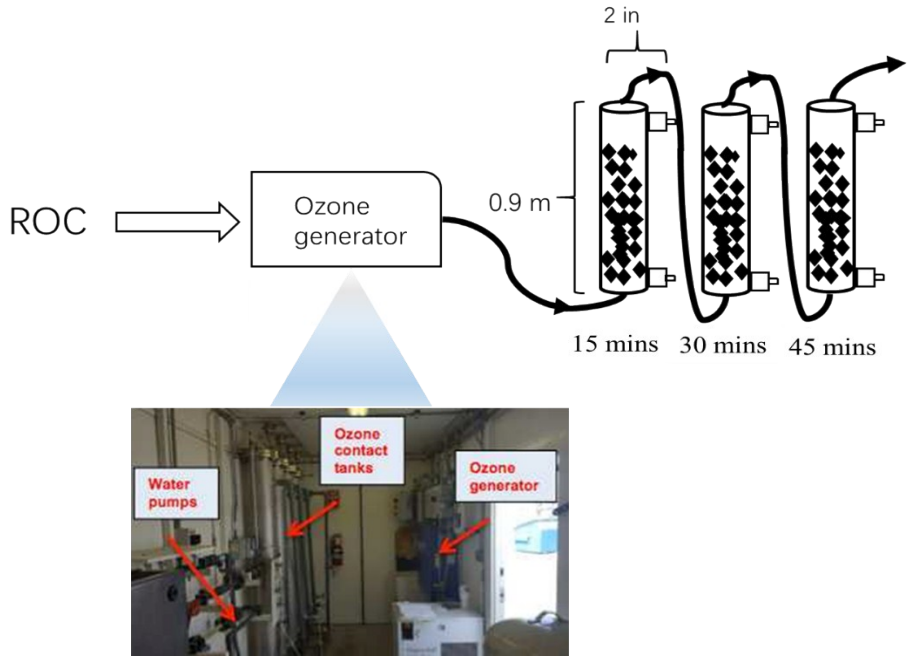

Fig. S1. Schematic diagram of the pilot-scale O_3/BAC system.

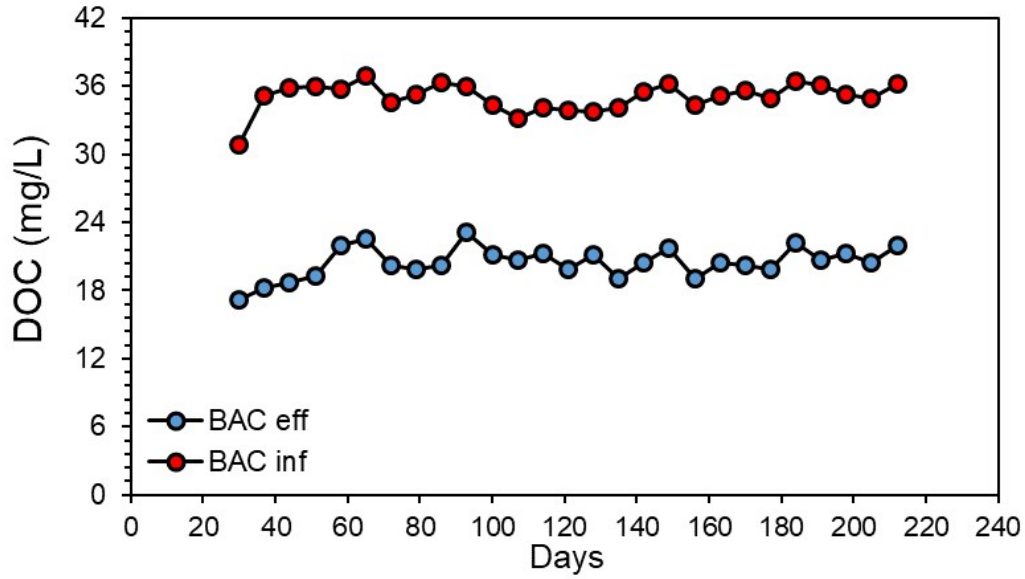

Fig. S2. DOC removal during BAC treatment (45 min EBCT) of O_3-treated (20 mg/L (~0.5 mg O_3/mg DOC)) RO concentrate during BAC column acclimatization.

Text S1. Analytical methods for pesticides and pharmaceuticals

Chemicals and reagents. HPLC-grade organic solvents (methanol, acetonitrile) and water were purchased from Thermo Fisher Scientific. Analytical standards of imidacloprid, fipronil, fipronil desulfinyl, DEET, atenolol, sulfamethoxazole and deuterated imidacloprid-d_4, atenolol-d_7, DEET-d_{10} were obtained from Sigma-Aldrich. Analytical standards of fipronil sulfide and sulfone, were obtained from Bayer and BASF. Deuterated sulfamethoxazole-d_4, and mass-labeled [$^{13}C_2{}^{15}N_2$] fipronil and [$^{13}C_4{}^{15}N_2$] fipronil sulfone were bought from Toronto Research Chemicals and Cambridge Isotope Laboratories, respectively.

Sample extraction. Water samples were collected in 2 L glass bottles that had been baked at 400 °C for 3 h in a muffle oven, and were sealed with Teflon-lined caps. The samples were stored in the 4 °C cold room before extraction and sample extractions were completed within one week. Imidacloprid, fipronil, fipronil sulfone, fipronil sulfide and fipronil desulfinyl were extracted with Strata-X 33µm polymeric reversed-phased SPE cartridges (500 mg, 3 mL) obtained from Phenomenex (Torrance, CA, USA). Twenty ng of imidacloprid-d_4 and mass-labeled [$^{13}C_2{}^{15}N_2$] fipronil and [$^{13}C_4{}^{15}N_2$] fipronil sulfone were spiked into 500-mL water samples. The SPE cartridges were pre-conditioned with 6 mL acetonitrile followed by 6 mL HPLC water. Then spiked water samples were loaded on the cartridges at 2-3 mL/min. After loading, cartridges were washed with 6 mL methanol/water mixture (60:40, v/v) and then dried under a gentle nitrogen stream. The target compounds were eluted with 10 mL acetonitrile and the elution was concentrated by nitrogen blow-down to 0.5 mL for LC-MS/MS analysis.

DEET, atenolol and sulfamethoxazole (SMX) were extracted with Supel^{TM}-Select HLB SPE cartridges (200 mg, 6 mL) purchased from Supelco (Bellefonte, PA, USA). Fifty ng of DEET-d_{10}, atenolol-d_7 and sulfamethoxazole-d_4 were spiked into 500-mL water samples. The SPE cartridges were pre-conditioned with 6 mL methanol followed by 6 mL HPLC water. The water samples were passed through the cartridges at 2-3 mL/min. Cartridges were then washed with 6 mL water and dried under a gentle nitrogen stream. The target compounds were eluted with 10 mL methanol and the elution was concentrated to 0.5 mL by nitrogen blow-down for LC-MS/MS analysis.

LC-MS/MS analysis. Target compounds were quantified on a LC-MS/MS triple quadrupole system (Agilent) equipped with a 150 mm × 3 mm Synergi 4 µm Hydro-RP 80 Å column (Phenomenex, Torrance, CA, USA). Compounds were separated using a 43 min gradient method at a 0.6 mL/min flowrate. The mobile phases A and B were water with 5 mM ammonium formate and methanol, respectively. The gradient is shown in the Table S2. The injection volume was 10 µL. Electrospray ionization was used to detect the compounds with the following operational parameters: capillary voltage 3500 V in both positive and negative; nebulizer pressure 45 psig; drying gas 7 L/min; gas temperature 300 °C; sheath gas flow 9 L/min; sheath gas temperature 250 °C; nozzle voltage 500 V in both positive and negative ion mode. Compound specific parameters are listed in Table S3. The method reporting limits were 10 ng/L for the pesticides and pharmaceuticals and 1 ng/L for the fipronil transformation products.

Table S1. Gradient method parameters. A = water with 5 mM ammonium formate, B = methanol.

Time (min)	A (%)	B (%)
0	95	5
2	95	5
10	58	42
12	58	42
13	23	77
19	23	77
27	10	90
32	10	90
33	0	100
38	0	100
41	95	5
43	95	5

Table S2. Optimized LC-MS/MS parameters for the analytes by MRM.

Compound	MRM transition	Dwell (ms)	Fragmentor (V)	Collison Energy (V)	Cell Accelerator Voltage (V)	Polarity
Fipronil	435.0/330.0	50	112	8	7	Negative
Fipronil sulfone	450.9/414.9	25	140	5	7	Negative
Fipronil sulfide	418.9/382.9	25	110	5	7	Negative
Fipronil desulfinyl	387.0/351.0	25	80	5	7	Negative
[$^{13}C_2{}^{15}N_2$] Fipronil	439.0/334.0	50	112	8	7	Negative
[$^{13}C_4{}^{15}N_2$] fipronil sulfone	456.9/420.9	25	140	5	7	Negative
Imidacloprid	256.1/209.1	50	110	9	7	Positive
Imidacloprid-d_4	260.1/213.1	50	110	9	7	Positive
Sulfamethoxazole	254.0/92.0	7	110	25	7	Positive
Atenolol	267.0/145.0	7	130	24	7	Positive
DEET	192.0/119.0	100	110	15	7	Positive
Sulfamethoxazole-d_4	258.0/96.0	7	110	25	7	Positive
Atenolol-d_7	274.0/145.0	7	130	24	7	Positive
DEET-d_{10}	202.0/119.0	100	110	15	7	Positive

Table S3. Concentrations (average ± range of duplicate sample events) for emerging contaminants at different O_3 doses and BAC EBCTs.

Exp. Condition	Conc. (ng/L)	EBCT (min)					Removal
		Pre-O_3	BAC Inf.	15	30	45	(%)
No ozonation	Imidacloprid	-	427±51	344±37	183±21	51±3	88±0.7
	Fipronil	-	179±21	155±14	72±9	20±5	89±1.5
	Atenolol	-	2446±367	1986±417	1007±171	337±44	86±0.3
	SMX	-	2495±374	2454±270	2396±216	2316±266	7±3.3
	DEET	-	255±54	237±40	193±25	103±11	59±4.2
0.5 mg O_3/mg DOC	Imidacloprid	531±74	393±43	92±7	11±1	ND	100
	Fipronil	165±17	91±6	21±5	3±1	ND	100
	Atenolol	1324±197	555±28	500±56	331±110	63±26	95±0.2
	SMX	1417±104	272±55	468±88	268±47	256±20	82±0.1
	DEET	100±36	78±20	54±21	42±15	25±6	74±3.6
1.0 mg O_3/mg DOC	Imidacloprid	480±37	236±41	65±15	ND	ND	100
	Fipronil	217±30	32±5	4±1	ND	ND	100
	Atenolol	1659±365	179±21	210±27	136±20	19±1	99±0.2
	SMX	1734±75	122±44	201±9	139±3	92±21	95±1
	DEET	661±98	316±58	228±54	172±43	103±12	84±0.5
0.5 mg O_3/mg DOC with methanol	Imidacloprid	573±57	430±65	75±7	7±0.4	ND	100
	Fipronil	192±25	94±8	15±2.4	2±0.3	ND	100
	Atenolol	1277±268	834±184	484±126	125±28	47±13	96±0.2
	SMX	1273±230	234±21	284±26	225±61	176±14	86±1.4
	DEET	111±11	86±14	41±6	26±4	15±1	86±0.4

ND = Not Detectable.

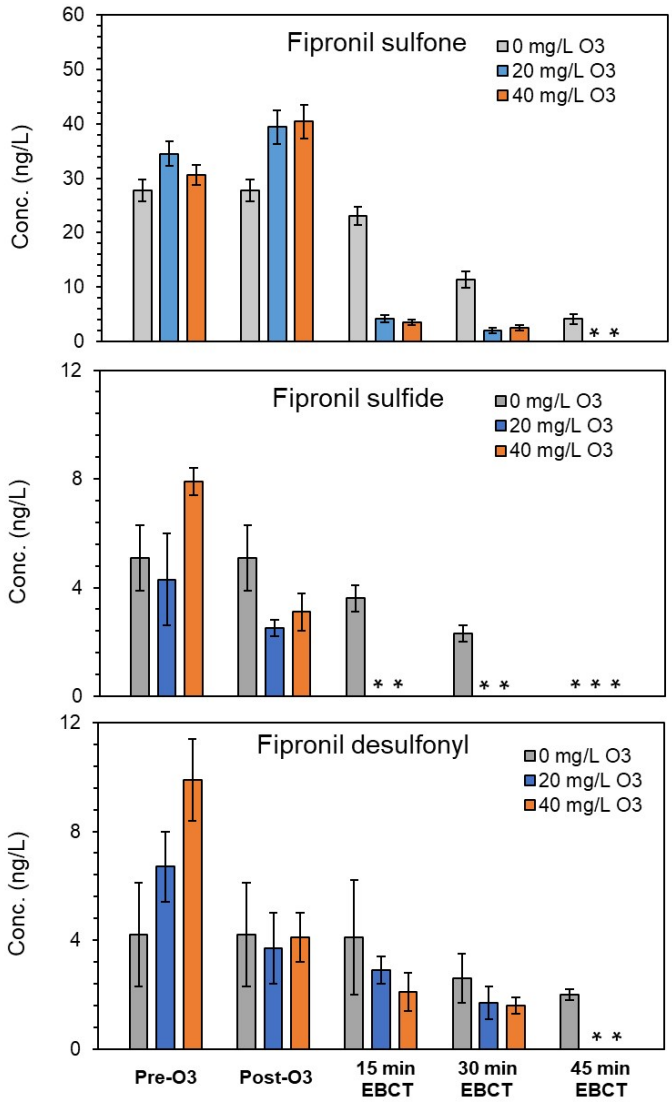

Fig. S3. Concentrations of fipronil sulfone, fipronil sulfide and fipronil desulfonyl at different BAC EBCTs during O_3/BAC treatment with different O_3 doses. Error bars represent the range of duplicate samples collected on separate occasions. * = below the reporting limits (< 1 ng/L).

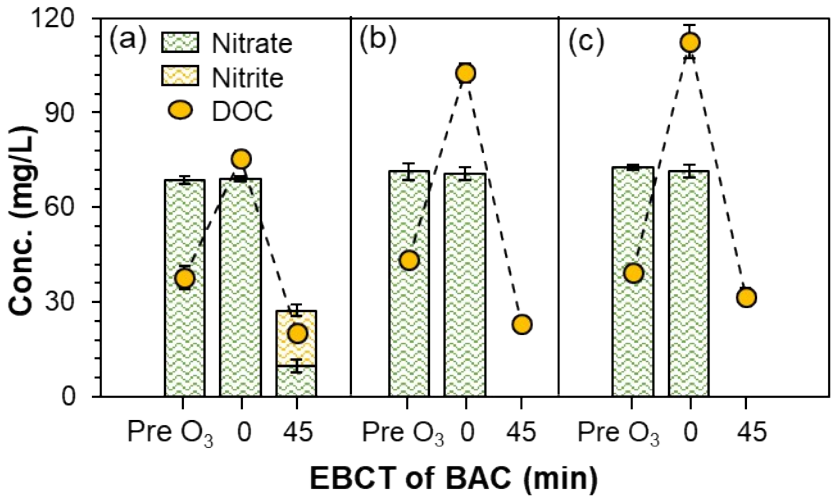

Fig. S4. Concentrations of DOC (mg-C/L), nitrite (mg-N/L) and nitrate (mg-N/L) at different BAC EBCTs after pre-treatment with 0.5 mg O_3/mg DOC and addition of (a) 40 mg-C/L, (b) 60 mg-C/L and (c) 70 mg-C/L methanol. Error bars represent the range of duplicate samples collected on separate occasions.